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A preservation study of carbon nanotubes in alumina-based nanocomposites via Raman spectroscopy and nuclear magnetic resonance

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ABSTRACT Raman spectroscopy was used to study the preservation of the carbon nanotube structure in nanotube-reinforced alumina nanocomposites consolidated via spark plasma sintering (SPS). A series of Raman spectroscopy experiments was used to identify the thermal breakdown temperature of single-walled carbon nanotubes (SWCNTs) embedded in nanocrystalline alumina. It was found that the carbon nanotube structure remains intact after sintering at 1150 °C, but almost completely breaks down by 1350 °C after only 5 min. Also, ²⁷Al nuclear magnetic resonance (NMR) was used to study the chemical and structural effects of high-energy ball milling (HEBM) and SPS consolidation on pure alumina and SWCNT-alumina nanocomposites. HEBM does not change the mixed coordination number of the as-received alumina, but slight peak shifts indicate residual stresses. No Al₄C₃ was detected in any of the consolidated samples – even up to 1550 °C for 10 min. Thus, it is concluded that consolidation of carbon nanotube-reinforced composites should be completed at temperatures below ~ 1250 °C in order to preserve the carbon nanotube structure.

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1 Introduction

There is growing interest in ceramic matrix nanocomposites (CMCs) reinforced with carbon nanotubes for structural and armor applications. The main obstacle in using CMCs in applications traditionally utilizing metals and alloys is their low fracture toughness and uncertain mechanical performance due to catastrophic failure. Many researchers have reported on carbon nanotube-reinforced CMCs, but few have experimentally confirmed the preservation of the nanotubes after high temperature consolidation. This fact may indeed be partially responsible for the inconsistencies of reported results and explain the reason why some researchers find that carbon nanotube

additions benefit mechanical properties [1–5] and why others do not [6, 7]. In this study, we investigate the microstructure of alumina nanocomposites reinforced with 5–10 vol. % single-walled carbon nanotube (SWCNTs) fabricated via spark plasma sintering (SPS).

In this study, constant and pulsed laser Raman spectroscopy was used to verify the preservation of the carbon nanotubes in alumina-based nanocomposites fabricated for 3 to 5 min at 1150–1200 °C, and to identify the temperature over which the nanotube structure is destroyed. SPS was used for consolidation because it avoids the excessive grain growth that would prevent attainment of a truly nanocrystalline material; it is an advanced pressure-

assisted consolidation technique that can produce fully dense samples at lower temperatures and shorter times than conventional sintering techniques would allow. Although the mechanisms behind SPS are unclear, it is believed that a combination of rapid heating rate, pressure application, and electrical pulsing enhances surface diffusion and thus promotes the sintering of the ceramic powders [8, 9].

In addition to Raman spectroscopy, a few SPS samples were pulverized and nuclear magnetic resonance (NMR) was conducted to investigate whether aluminum carbide (Al₄C₃), a brittle compound potentially detrimental to nanocomposite strength/toughness, was formed during SPS consolidation. A series of spectra were taken to investigate the local chemical environment of consolidated alumina and CNT-alumina composites. In addition, information about the interface between the carbon nanotubes and the alumina matrix was discovered in this investigation. The formation of Al₄C₃ could only occur if the bonds within the single wall of the nanotube were broken and new bonds formed between metallic aluminum atoms. Reduction of Al₂O₃ to metallic aluminum is possible during SPS due to a reducing environment, but is unlikely due to the thermal stability of alumina. Nonetheless, SPS is known to enhance sintering and the effects on kinetics of chemical reactions are unknown. Although the formation of aluminum carbide may be slow under equilibrium conditions, it may be accelerated within the SPS. NMR provided an indirect method to determine whether the carbon nano-

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tube structure was preserved during consolidation.

2 Experimental procedures

2.1 Powder processing of SWCNT-alumina powder

Before use, as received alumina powder (Nanotek, 32 nm) was high-energy ball milled (HEBM) in order to induce residual strain for faster, lower temperature sintering. About 10 g of alumina powder and 1 wt. % poly vinyl alcohol (PVA) were loaded into a tungsten-carbide (WC) vial with a single 14-mm diameter WC ball and HEBM for 24 h in a Spex 8000 Mixer/Mill. The PVA was added to prevent agglomeration during milling and was baked off at 350 °C for 3 h in air after milling. The single-walled carbon nanotubes (SWCNTs) used in this study were produced via HiPco method (Carbon Nanotechnologies, Inc., Texas, ~ 1–4 nm diameter, ~ 1 μm length, > 90% purity). The appropriate amount of SWCNTs was weighed out and dispersed in ~ 200 ml of ethanol and ultrasonicated for 15 min. The balance amount of HEBM alumina was added to ~ 250 ml of ethanol while hand-stirring and ultrasonicated for 15 min. The two slurries were slowly combined while hand stirring and ultrasonicated for an additional 15 min. The composite slurry was added to a polystyrene bottle containing zirconia ball media (~ 1/3 by volume) and wet-milled for 24 h. The wet-milled slurry was then dried by evaporation on a hot plate with a magnetic stir bar. The dry powders were crushed with a mortar and pestle and sieved through 150 μm mesh.

2.2 Spark plasma sintering (SPS)

The final composite powders are consolidated in the SPS at 1150 °C for up to 8 min to yield fully dense compacts (98%–100%TD). Consolidation was performed under vacuum in the Dr. Sinter 1050 SPS machine. The following processing parameters were used: 105 MPa of applied pressure, and “on” pulse of 12 cycles of 2 ms each and a “off” interval between pulses of 2 cycles, a maximum pulse settings of 5000 A and 10 V, and a pressure of 105 MPa. An optical pyrometer was used to measure temperature and a heating rate of 125 °C/min was used

from room temperature to 600 °C. From 600 °C to the desired final set point (1150–1550 °C in this study), heating rates ranged from 150 °C/min to 233 °C/min. Density was determined via Archimedes immersion method and consolidated samples had dimensions of 19 mm in diameter and 3–4 mm in thickness.

2.3 Raman spectroscopy

Raman spectroscopy was used to verify that the carbon nanotubes were preserved during the processing steps. Both constant and pulsed laser Raman spectroscopy was used in this study. Pulsed laser Raman spectroscopy was conducted at Lawrence Berkeley National Laboratory. Spectra were detected with an imaging photomultiplier (1024 × 1024) with 5 cm⁻¹ resolution. First, an investigation into the preservation of 10 vol. % SWCNT-alumina consolidated at 1150 °C for 3 min was conducted using lasers of 522–488 nm wavelength with a 60 s scan. Four scans were taken and overlaid for comparison of *D*- and *G*-bands: pure SWCNTs, graphite standard, pure alumina, and the 10 vol. % SWCNT-alumina composite. Using the same equipment, we performed a more in-depth Raman study to identify the highest SPS condition that can be used without destroying the carbon nanotubes using a 488 nm Ar⁺ laser line at a power of 35 mW and collection times of 4 min.

Furthermore, the nanocomposites were studied with a constant laser source

Raman spectrometer at University of California, Davis. Raman spectra were obtained for pure SWCNTs, 10 vol. % SWCNT-alumina nanocomposite, 5 vol. % SWCNT-alumina nanocomposite, and pure alumina. A 1064-nm YAG laser was used for Raman spectra acquisition and laser power varied from 50 mV for the pure SWCNTs and 100 mV for pure and composite alumina samples.

2.4 Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (NMR) was also used to investigate the carbon nanotube-alumina nanocomposites. Consolidated samples were crushed and sieved through 150 μm mesh to yield powders fit for NMR study.²⁷ Al magic angle spinning (MAS) NMR experiments were carried out on a Bruker Avance 500 widebore system, with the Larmor frequency of 130.32 MHz, an MAS rate of 15 kHz, a digitization rate of 166.7 kHz, a pulse length of 0.5 μs (15° tip angle) and 1 s of recycle delay, and transients of 1024. The system was calibrated with aluminum chloride solution and ~ 100 mg of powder were loaded into a 2.5-mm vial and analyzed under an 11.74 T magnetic field.

3 Results and discussion

The results from the pulsed laser Raman spectroscopy are shown in Figs. 1 and 2. Comparison of the spectra in Fig. 1 for pure SWCNT and the

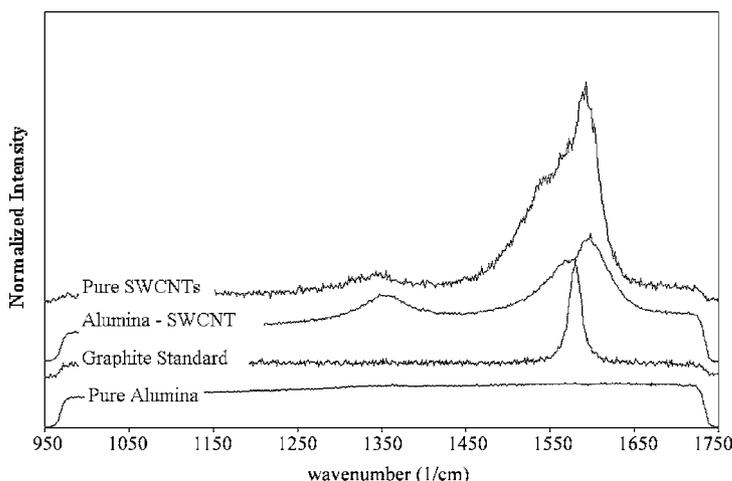


FIGURE 1 Pulsed laser Raman spectroscopy comparing graphite, SWCNT and alumina starting powders with our 10 vol. % SWCNT-alumina nanocomposite (SPS: 1150 °C, 3 min)

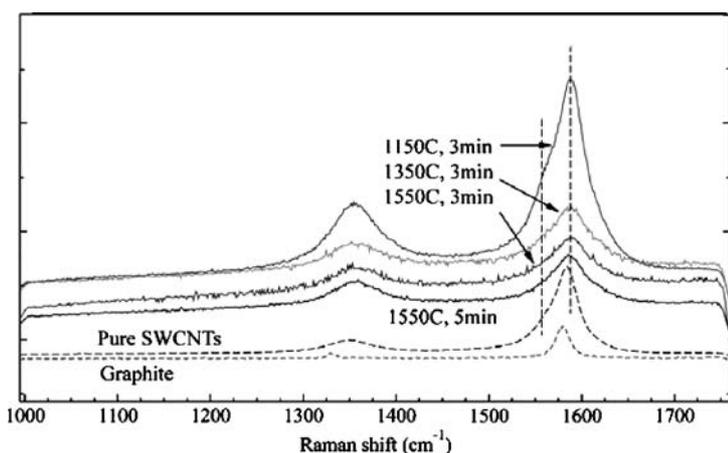


FIGURE 2 Pulsed laser Raman study of SWCNT-alumina nanocomposites for determination of carbon nanotube degradation temperature as a function of SPS temperature and time

nanocomposite consolidated at 1150 °C reveals a major peak at $\sim 1595 \text{ cm}^{-1}$ and a shoulder in the 1550–1575 cm^{-1} region in both spectra. This is termed the “G-band” is the tangential shear mode of the carbon atoms. The “peak splitting” of this band reflects the overlap of electrons within the graphene layers when one rolls these sheets into tubes. Thus, although the graphite peak is located in the same position as the SWCNT spectrum, it does not have splitting or a shoulder. Therefore, presence of splitting of the “G-band” indicates a nanotube structure. The minor peak at $\sim 1350 \text{ cm}^{-1}$ is caused by defects and the presence of amorphous carbon and can be used to quantify the purity of processed carbon nanotubes [10, 11]. Clearly, the unique structure of carbon nanotubes is intact

after SPS consolidation at 1150 °C for 3 min.

A more in-depth Raman study was performed to identify the highest SPS condition that can be used without destroying the carbon nanotubes. A series of spectra were taken with a 488-nm laser source at various laser powers ranging from 25 mW to 100 mW, as shown in Fig. 2. The same G-band peak splitting is seen in the lowest temperature spectra representing consolidation at 1150 °C, as located by the left dashed line. Careful analysis of Fig. 2 shows that the peak splitting disappears in the spectrum representing consolidation at 1350 °C, indicating the loss of the nanotube structure. Thus, carbon-nanotube reinforced CMCs should be consolidated at temperatures below $\sim 1250 \text{ }^\circ\text{C}$. This is con-

sistent with Flahaut et al.’s findings in situ grown CNT-Fe-alumina nanocomposites fabricated via hot pressing [7].

Furthermore, the nanocomposites were studied with a constant laser source Raman spectrometer. Figure 3 contains Raman spectra for pure SWCNTs, 10 vol. % SWCNT-alumina nanocomposite (SPSed at 1250 °C for 3 min), 5 vol. % SWCNT-alumina nanocomposite (SPSed at 1200 °C for 10 min), and pure alumina (SPSed at 1200 °C for 3 min). This spectrometer was more sensitive to small shifts in wavenumber and in nanotube structure. The same G-bands and D-bands are observed here, in addition to the radial breathing modes (RBMs) at lower wavenumbers. The RBMs are located below 500 cm^{-1} and only are possible in tubular graphite. The study of RBMs can provide information about nanotube chirality (i.e., (n, m) indices) and diameter distributions since the RBM frequency is inversely proportional to nanotube diameter [12]. In this study, diameter information was not extracted because multiple laser lines were not taken. Nonetheless, the presence of RBMs in our samples consolidated at as high as 1250 °C in the SPS verifies the presence of carbon nanotubes in our nanocomposites.

Analysis of the NMR spectra in Fig. 4a reveals that the aluminum atom coordination of the as-received powder was a mixture of four (at $\sim 65 \text{ ppm}$)

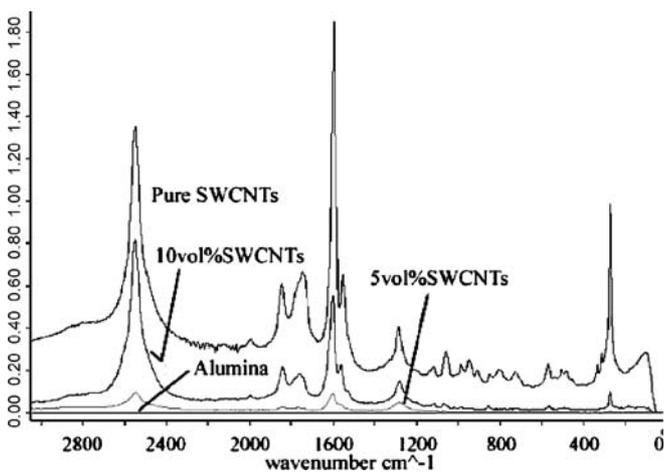


FIGURE 3 Constant source Raman spectroscopy, spectra (from top to bottom) of pure SWCNTs, 10 vol. % SWCNT-alumina nanocomposite, 5 vol. %, SWCNT-alumina nanocomposite, and pure alumina

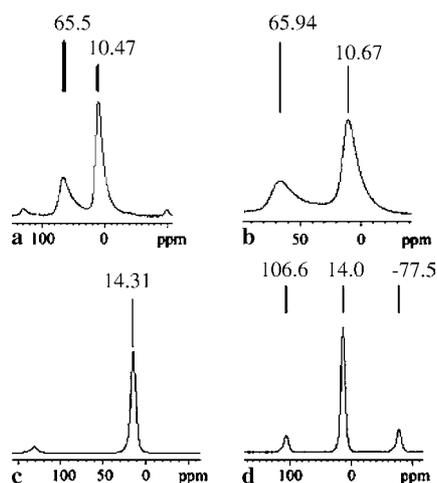


FIGURE 4 ^{27}Al MAS NMR spectra showing: (a) As-received alumina, (b) HEBMed alumina, (c) pure alumina SPSed at 1200 °C for 4 min, and (d) 5 vol. % SWCNT-alumina SPSed at 1200 °C for 6 min (10–14 ppm = 6 coordinated and $\sim 66 \text{ ppm}$ = 4 coordinated)

and six (at ~ 10 ppm). Close inspection of the 6-fold peak indicates that there is some distortion in the aluminum-oxygen octahedral structure due to the small amount of splitting at the top of this peak. HEBM seems to provide sufficient energy to correct this distortion because the HEBM spectra show a clean 6-fold peak (Fig. 4b). Consequently, consolidation in the SPS at 1200°C results in complete phase transformation of the cubic 4-coordinated, metastable alumina gamma phase to the rhombohedral 6-coordinated, stable alpha phase as seen in Fig. 4c–d. The two satellite peaks in Fig. 4d are termed “spinning side bands” and are a result of spinning and are not indicative of the chemical environment of aluminum atoms.

In addition, analysis of the carbon nanotube/alumina composite spectra for both 1200°C and 1550°C (not shown) indicate that the alumina remains 6-coordinated and that no aluminum carbide (Al_4C_3) was formed. A peak between 20–100 ppm would appear if aluminum carbide were formed. In other words, the composite sample is purely a physical mixture and no chemical bonding is occurring at the alumina grain/carbon nanotube interface. This is an important observation because formation of Al_4C_3 would mean breakdown of the nanotube, because of the nanotubes used in these studies are single-walled. Thus, the nanotubes re-

main as ultra-strong reinforcing fibers within the brittle alumina matrix.

4 Conclusions

SWCNT-reinforced alumina nanocomposites were characterized using Raman spectroscopy and NMR techniques to discern whether the nanotube structure was retained after SPS consolidation to full density. Preservation of strong carbon nanotube structure is important for the improvement of mechanical properties, specifically the fracture toughness, in brittle ceramic matrices. With Raman spectroscopy, it was found that the carbon nanotube structure was preserved in alumina nanocomposites at SPS sintering temperatures up to $\sim 1250^\circ\text{C}$. Comparison of the 1150°C and 1350°C spectra reveal that carbon nanotubes break down somewhere between these two sintering temperatures – it is thus advised that sintering temperatures be limited to $\sim 1250^\circ\text{C}$. NMR data reveal that no Al_4C_3 is formed during sintering even up to temperatures of 1550°C for 10 min. Thus, the single wall of the carbon nanotubes remains intact and is capable of maximum reinforcement and load-bearing capacity. The inconsistencies in literature regarding the effects of addition carbon nanotubes to alumina may be attributed to high sintering temperatures of composites –

where retainment of carbon nanotubes is questionable.

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